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Some applications of vibrational spectroscopy in conformational analysis

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Abstract

We report some vibrational spectroscopic approaches to studying conformational equilibria and kinetics, which were developed in recent years: (i) investigation of relative band dichroism in polarized IR spectra of crystals; (ii) kinetic investigations of conformational transitions in liquid solutions; and (iii) use of conformationally inhomogeneous compounds as probes for studying molecular mobility and free volume distribution in polymers.

Keywords: IR spectra; Conformations; Dichroism; Molecular mobility; Polymer

1. Introduction

Physical methods are widely used in solving problems of conformational analysis. Vibrational spectroscopy is one of the most effective methods in this field [1,2]. We report some new vibrational spectroscopic approaches to conformational problems, which were developed in our group.

2. Results and discussion

2.1. Determination of the molecular conformation in crystals by relative IR band dichroism

To determine molecular conformations one may use data on the IR band dichroism of molecular crystals [3]. For example, rotation of CH_2X- and CH_2Y-groups in 1,2-disubstituted ethane results in *trans* and *gauche* conformations. Let us distinguish the vibrational modes ν_1 and ν_2, with ν_1 being a characteristic vibration of some set of internal coordinates of the CH_2X-part of the molecule, and ν_2 that of the CH_2Y-part. Directions of the dipole transition moments, $\partial\overline{\mu}/\partial Q_i$, of the ν_1 and ν_2 modes may be determined on the basis of the assignment of vibrations. For IR spectra of the crystal obtained using polarized incident beam, the intensity of the ith band $I(\nu_i)$ depends, on the orientation of the polarisation plane with respect to the sample (it is characterised by an angle ϑ). $I(\nu_i)$ reaches a maximum (or minimum) value $I_{max}(\nu_i)$ (or $I_{min}(\nu_i)$) at an angle $\vartheta_{max}(\nu_i)$ (or $\vartheta_{min}(\nu_i)$). A comparison of experimental values $\vartheta_{max}(\nu_i)$ and $\vartheta_{min}(\nu_i)$ for the chosen bands with the values ϑ, expected for possible conformations, enables one to determine the conformation of molecules in the crystal. The samples under investigation were thin (~ 0.01 mm) crystalline films between windows made of KBr. As an example, Fig. 1 shows IR spectra of sulphone $ClC_6H_4SO_2CH_2Br$, obtained using beems with interperpendicular

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